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14. ABSTRACT

Much of the on-going research in microbiologically influenced corrosion (MIC) is directed at identification of unifying mechanisms for global observations of MIC-related phenomena, e.g., ennoblement of passive alloys and corrosion of carbon steel pilings. Both occur in fresh and saline waters. In the following sections data will be presented suggesting that a single explanation for either is unsatisfactory. The two examples provide evidence that MIC mechanisms can be site specific and multiple mechanisms can be operative, especially in coastal waters where water chemistry varies with location and is subject to riverine inputs and tidal fluxes.

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MICROBIOLOGICALLY INFLUENCED CORROSION: GLOBAL PHENOMENA, LOCAL MECHANISMS

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SUMMARY: Much of the on-going research in microbiologically influenced corrosion (MIC) is directed at identification of unifying mechanisms for global observations of MIC-related phenomena, e.g., ennoblement of passive alloys and corrosion of carbon steel pilings. Both occur in fresh and saline waters. In the following sections data will be presented suggesting that a single explanation for either is unsatisfactory. The two examples provide evidence that MIC mechanisms can be site specific and multiple mechanisms can be operative, especially in coastal waters where water chemistry varies with location and is subject to riverine inputs and tidal fluxes.

Keywords: ennoblement, ALWC, MIC

1. ENNOBLEMENT

Ennoblement of the open circuit potential (E_{corr}) of passive alloys, a shift in the positive direction, as a result of biofilm formation is a global phenomenon and has been reported in fresh, brackish and seawaters (Little et al. 2008). Theoretically, E_{corr} ennoblement should increase the probability for pitting and crevice corrosion initiation and propagation of some passive alloys, particularly those alloys for which the pitting potential is close to E_{corr}. Numerous researchers have shown that increased cathodic reduction rates accompany ennoblement of E_{corr} (Scotto et al. 1985; Motoda et al. 1990; Mollica 1992; Zhang and Dexter 1995). However, attempts to relate ennoblement to a single microbiologically mediated mechanism have failed.

Comparison of ennoblement data from different locations and different investigators is complicated because extent of ennoblement is affected by sample size, flow rate and temperature (Little et al. 2008). Ennoblement has been measured for metals boldly exposed, metals incorporated in crevice assemblies and polarized metals. The alloys tested include, but are not limited to: UNS S30400, S30403, S31600, S31603, S31703, S31803, N08904, N08367, S44660, S20910, S44735, N10276, N06625, platinum, gold, palladium, chromium, titanium, and nickel.

In fresh water, ennoblement can be the result of microbial deposition of manganese and localized corrosion has been related directly to the biomineralized deposits on the surface of 300 series stainless steels (Linhardt 1994; Dickinson et al. 1996; Renner 1996). Dexter *et al.* (2003) reported that manganese was found within biofilms on Nitronic 50 (UNS S20910) coupons exposed in Delaware Bay. Delaware Bay is an estuary, strongly influenced by the Delaware River. Water at this location has been referred to as both marine and coastal seawater (Dexter and Zhang 1990; Zhang and Dexter 1995). Salinity varies from 26 to 33 ppt and the temperature from 20 to 28 °C. Manganese distribution maps prepared by the U.S. Geological survey (Dickinson and Pick 2002) indicate that manganese concentration in the Delaware River basin is high. Therefore, E_{corr} ennoblement in Delaware Bay may be due to microbial manganese deposition and the data generated at that site may have little in common with data collected from other coastal locations. Manganese is not routinely reported in marine biofilms associated with ennoblement.

Martin *et al.* (2007) compared ennoblement of several alloys at two coastal seawater locations – Key West, Florida and Delaware Bay (Figures 1a & 1b). The two locations have different temperatures and different salinities. Martin *et al.* (2007) demonstrated that E_{corr} ennoblement is site specific, varying 100 mV vs. saturated calomel electrode (SCE) between locations, with higher potentials at Delaware Bay. Localized corrosion was observed for alloy SS3040 exposed in Key West, but not in Delaware Bay.

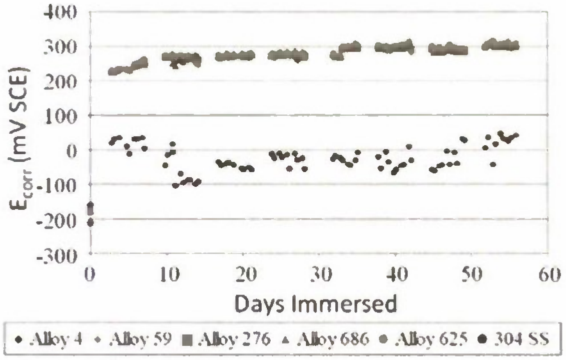

Figure 1a. E_{corr} of Ni-Cr-Mo alloys and 304SS during 60-day exposure at Key West, showing corrosion potential ennoblement approaching 300 mV SCE in the first 30 days (Martin et al. 2007).

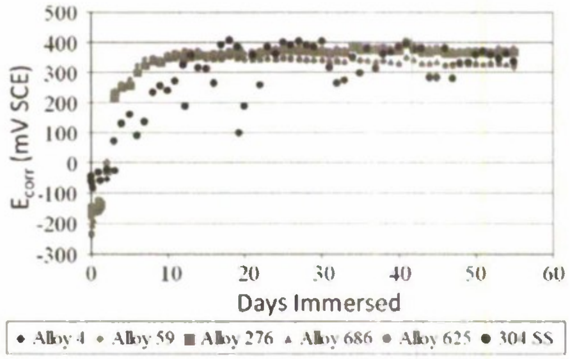

Figure 1b. E_{corr} of Ni-Cr-Mo alloys and 304SS during 60-day exposure at Delaware Bay, showing corrosion potential ennoblement approaching 300 mV SCE in the first 7 days (Martin et al. 2007).

Several mechanistic explanations have been proposed for ennoblement in marine waters. Little and Mansfeld *et al.* (1994) categorized the proposed mechanisms into three categories: thermodynamic, kinetic, and alteration of the nature of the reduction reaction itself. Thermodynamic arguments for ennoblement suggest that either a pH decrease at the metal/biofilm interface or a local increase of the partial pressure of oxygen (pO_2) raises the reversible potential of the oxygen electrode (E^0O_2) (Figure 2). For aerobic biofilms, changes in E^0O_2 due to changes in pO_2 would be small. For seawater, a decrease of local pH from 8 to 3 would account for an ennoblement of about 300 mV, assuming that the exchange current density for the oxygen reduction reaction (i^0O_2) and the cathodic Tafel slope remain constant (Figure 2) where the initial E^1_{corr}, changes to E^2_{corr} as $E^{0,1}O_2$ increases to $E^{0,2}O_2$.

Little *et al.* (1991) measured E_{pit} in abiotic chloride solutions at pH = 4 and 2 and observed that E_{pit} decreased below ennobled E_{corr} values determined in natural seawater, and therefore dismissed the possibility that ennoblement is due to reduction of surface pH. This conclusion was challenged by Chandrasekaran and Dexter (Chandrasekaran and Dexter 1993) who suggested that E_{pit} for a stainless steel covered by a biofilm might be different from that measured in an abiotic solution. Nevertheless, the same authors conceded, "all the observed ennoblement on stainless steel, particularly in low salinity waters, cannot be explained by pH alone." Mollica *et al.* (Mollica et al. 1990) analyzing field test data, concluded, "the phenomenon of oxygen depolarization on active-passive alloys covered by slime does not depend on acidification of the substrate but, on the contrary, on a light (sic) alkalization."

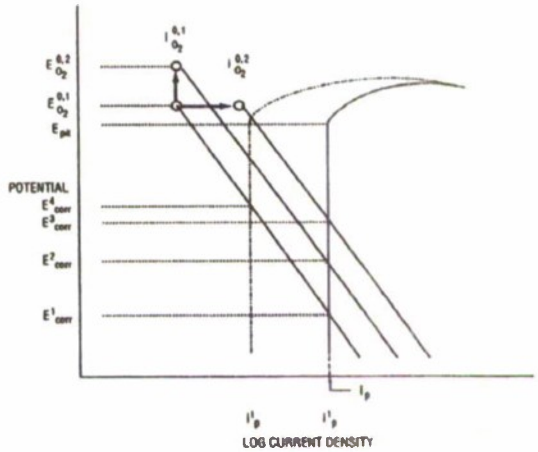

Figure 2. Schematic polarization curves for stainless steel in seawater (Little and Mansfeld 1994).

Kinetic arguments for ennoblement suggest that the rate of oxygen reduction at a given potential (E) can also increase due to an increase of i^0O_2 leading to an increase of E^1_{corr} to E^3_{corr} (Figure 2). Dexter and Gao (1988) suggested that increased oxygen reduction rates might be due to an increase of i^0O_2, mediated by biopolymer metal complexes known to catalyze oxygen reduction. The nature of these organometallic catalysts has been the topic of wide discussion. Scotto *et al.* (1985) attributed catalysis to the presence of microbial enzymes and based this assertion on the abrupt drop in ennobled E_{corr} that accompanied addition of a respiratory inhibitor, sodium azide, to a microbial film. Srinivasan *et al.* (1985) pointed out the ability of enzymes to accelerate electrochemical reactions and noted the inhibitory effect of sodium azide on enzyme electrocatalysis of oxygen reduction. They further reported that lactase increased i^0O_2 on platinum approximately 40 times above that observed in the absence of the enzyme. Johnsen and Bardal (1985) observed that the presence of a biofilm dramatically increased the current density required to polarize stainless steel to a potential of -400 mV (SCE), adequate to provide cathodic protection in seawater. They attributed this increase to a lack of calcareous deposits and an enhanced oxygen reduction rate beneath the biofilm due to an increase of i^0O_2. The mechanism of organometallic catalysis has been criticized, however, because ennoblement is also observed on more noble metals, including titanium and platinum, which lack transition elements thought to be necessary to form catalyzing complexes (Mansfeld et al.

1989). The nature of the passive layer has also been suggested to play a role in ennoblement by altering the reduction rate of oxygen (Le Bozec et al. 2001). Differences in the semicondutive properties of the passive film have also been suggested to affect an alloys susceptibility to ennoblement (Dexter and Maruthamuthu 2001; Martin et al. 2007).

In the previous discussion it was assumed that microorganisms change the rate of the cathodic reaction and for neutral, aerated solutions, the cathodic reaction is reduction of oxygen. It is possible that microorganisms change the rate-determining step in an electrochemical reaction or produce an entirely different mechanism. Chandrasekaran and Dexter (1993) suggested that reduction in surface pH and production of hydrogen peroxide (H_2O_2) at low oxygen concentration are important contributory factors for ennoblement. The contribution of H_2O_2 to ennoblement is related to its relatively noble thermodynamic potential at low pH. Theoretically, at pH = 2.9 and pO_2 = 0.5 ppm, the presence of 8.2 mM H_2O_2 would produce an increase in the reversible potential of 0.5 V. These specific conditions have not been measured in an actual biofilm. Chandrasekaran and Dexter (1993) measured H_2O_2 concentrations ranging from 1.3 to 6.6 mM in biofilms on platinum coupons after a 1-year exposure. Feron *et al.* (1997) and Dupont *et al.* (1998) observed ennoblement of stainless steels exposed in "biochemical artificial seawater," artificial seawater amended with glucose and glucose oxidase. The enzyme catalyzes the oxidation of glucose to gluconic acid and H_2O_2 (Lai and Bergel 2002). Washizu *et al.* (2004) examined the role of H_2O_2 in ennobling biofilms by addition of catalase and perioxidase, enzymes known to decompose H_2O_2. Concentrations of 10-30 ppm H_2O_2 were identified in natural biofilms that produced ennobled E_{corr} values. Addition of catalase or peroxidase to the bulk solution decreased H_2O_2 concentrations to below 0.5 ppm and ennoblement was decreased resulting in E_{corr} values observed in sterile conditions. An important point should be made here. Previous work by Scotto *et al.* (1985) indicated that addition of sodium azide resulted in loss of ennoblement. In more recent work, Scotto and Lai (1998) report that catalase and peroxidase are reversibly inhibited by sodium azide. These results would seem to contradict, to some degree, the enzymatic mechanism of ennoblement. Addition of sodium azide to ennobled biofilms containing catalase or peroxidase would inhibit the decomposition of H_2O_2 and result in higher ennobled E_{corr} values, not a sharp decrease in E_{corr} values as reported earlier (Scotto and Lai 1998).

Theoretically it is also possible that E_{corr} becomes ennobled due to a decrease of passive current density (i_p) at constant E^0O_2, i^0O_2, and Tafel slope, leading to a change from E^1_{corr} to E^4_{corr} (Figure 2). Eashwar et al. (1995) proposed a mechanism in which siderophores (iron chelators) produced by microorganisms within biofilms at neutral pH act as inhibitors and enhance passivity of the stainless steel by reducing i_p (Figure 2). Siderophores, produced by all microorganisms, have been shown to possess excellent corrosion inhibition properties. McCafferty *et al.* (1995) demonstrated that a bacterial siderophore, parabactin, has an inhibitive effect on E_{pit} for aluminum in NaCl. Eashwar *et al.* (1995) predicted that siderophore production and maximum ennoblement occur at pH 8. Their proposed model has not been rigorously tested, but it does explain the observation by Scotto *et al.* (1985) of a drop in E_{corr} with the addition of sodium azide. The respiration inhibitor would prevent formation of siderophores. The theory involving enhanced passivation is also consistent with the observation that very noble E_{corr} values are often maintained for long periods of time without any indication of localized corrosion. Eashwar (1995) has called the theory "imaginary, but ... based on careful analysis of both the literature on ennoblement and ecological factors inherent in marine biofilms."

It has been reported in locations worldwide that ennoblement produced by natural biofilms increases the probability of pit and crevice initiation on a variety of passive alloys, as well as the rate of localized corrosion propagation. However, observations of ennobled E_{corr} alone cannot be used to predict an increased likelihood of localized corrosion for a crevice corrosion prone alloy, such as SS30400 stainless steel. Multiple mechanisms can be used to rationalize global observations of ennoblement in fresh water, estuarine and marine environments, but the mechanism for ennoblement at a particular location may be site-specific.

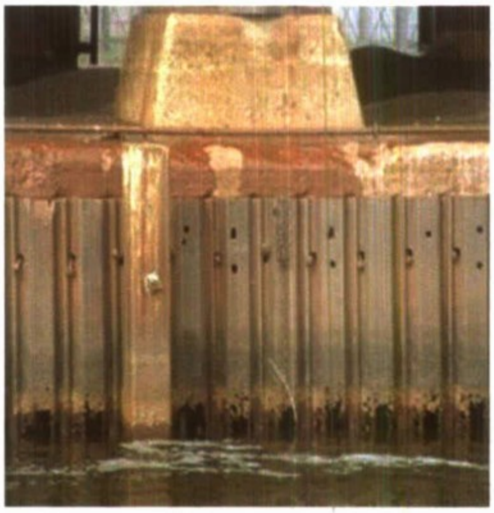

Figure 3. DSH pilling with visible perforation at the water line. Photograph reproduced with permission from Gene Clark, Sea Grant Program.

2. ACCELERATED LOW WATER CORROSION

Accelerated corrosion of carbon steel (CS) sheet pilings in estuarine and marine harbors is a global problem (Beech and Campbell 2008). The term "accelerated low water corrosion" (ALWC) is used to identify the phenomenon that is localized at or immediately below the low water level. ALWC is associated with thick corrosion products and large blisters and corrosion rates of 3 mm per year or higher have been reported. Recently accelerated corrosion of CS pilings was reported in Duluth-Superior Harbor (DSH), a fresh water estuary (Mitman 2006; Larsen 2008). Corrosion in DSH is associated with dense corrosion deposits or tubercles and rates are similar to those reported for ALWC. Carbon steel pilings in DSH that are over thirty years old are either completely or partially perforated by localized corrosion (Figure 3).

The detailed mechanism of ALWC in marine/estuarine environments continues to be a matter of some debate but several researchers have concluded that it is a form of microbiologically influenced corrosion (Gubner and Beech 1999; Gubner and Beech 1999; Beech and Campbell 2008). Gehrke and Sand (2003) completed a three-year study of pilings in German marine harbors with and without corrosion. They concluded that the ALWC was due to combination of sulfate-reducing bacteria (SRB) and thiobacilli in the fouling layers on the pilings. The sulfides produced by SRB in the anaerobic regions and sulfuric acid resulting from the thiobacilli in the aerobic regions combined to produce an extremely corrosive environment. Melchers and Jeffrey (2010) exposed mild steel coupons at 10 locations along the eastern Australian seaboard and concluded that corrosion below the mean low water level was more severe for higher average concentrations of total nitrogen concentration in the bulk seawater. They reported, "The increased occurrence of ALWC reported in recent years is most likely the result of elevated levels of water pollution in the waters to which the steel pilings has been exposed over its lifetime, irrespective of whether water pollution is currently decreasing." Melchers and Jeffrey (2010) did not link the corrosion to any specific organisms or mechanisms, but suggested that pollutants provided nutrients.

DSH is located at the extreme western end of Lake Superior and is described as a freshwater estuary. Kerfoot *et al.* (1999) described the Lake Superior watershed, "as an ecosystem that was disturbed earlier by turn-of-the-century mining in a patchwork manner along the shoreline. Portions of the lake are in a recovery phase, whereas other areas are still impacted by slow resuspension-deposition dynamics and continuing mining activities." Kerfoot and Robbins (1999) cite erosion of metal-rich ore bodies around Lake Superior as a source of copper enrichment in shoreline sediments. Lake Superior is a monomictic lake, meaning that during the summer it separates into two layers based on water density, then from fall to spring the layers are mixed together causing a cycling of elements. DSH is polymitic, i.e., seiches or free standing wave oscillations are almost always present, suspending particulates into the water column (Sydor 1978). DSH is icebound from mid-December to mid-April and during that time has a durable, well-defined ice cover. Freeze ice thicknesses in DSH range from 0.5 to 1.4 m in addition to snow ice, stack ice, and ice from wave and splash action along harbor walls (Scott et al. 2009).

Ray *et al.* (2009) reported that a combination of biological, chemical and physical events contribute to the corrosion of CS pilings in DSH. Iron-oxidizing bacteria (IOB) convert Fe^{+2} to Fe^{+3} creating dense deposits with anaerobic conditions beneath them. Copper, naturally occurring in DSH, precipitates at the base of the tubercles directly on the CS. The resulting galvanic cell produces aggressive localized corrosion. Ice scoring disrupts the tubercles and exposes localized areas of Cu-covered CS to O_2 and corrosion rates increase. The individual events in the sequence are predictable, but had not been previously reported. Furthermore the aggressive corrosion is directly related to specific microorganisms and water chemistry in DSH. Melchers and Jeffrey (2010) have suggested that ALWC and the events in DSH can be related to nutrients and the occurrence of MIC can be predicted based on concentration of nutrients in the water at a specific site, specifically nitrogen. The hypothesis has not been tested, but even if microbial growth is limited by nutrients, the hypothesis cannot provide site-specific mechanistic information.

3. CONCLUSIONS

MIC mechanisms for global phenomena can be site specific, depending on the microbial population and water chemistry. The most obvious differences in mechanisms for ennoblement and corrosion of carbon steel pilings are based on the differences between fresh and marine environments. Extent of ennoblement varies among locations and extent of ennoblement for a particular material cannot be used to predict an increased likelihood of localized corrosion for a crevice corrosion prone alloy, i.e. 304 stainless steel. Most experiments on ennoblement have been conducted in coastal environments. There may be site-specific environmental parameters, e.g., dissolved manganese and manganese depositing bacteria, which influence ennoblement. No single mechanism can be used to explain accelerated corrosion of carbon steel pilings around the world. There are obvious differences in the observations in DSH and reports of ALWC. ALWC is observed in the low water zone, just below the tidal zone, in saline waters containing gram per liter quantities of sulfate. DSH is a fresh water harbor with milligram per liter concentrations of sulfate. Corrosion in DSH is localized to the top 3 meters below the surface and water depth is not significantly influenced by tides. Furthermore, the IOB responsible for creating the conditions for copper deposition in DSH can cause corrosion via multiple mechanisms. The situation in DSH is directly related to the metals in the water.

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